IN THE UNITED STATES PATENT AND TRADEMARK OFFICE AS RECEIVING OFFICE

TITLE OF THE INVENTION

Coated Closure for Performing Direct Vial Surface Sorbent Microextraction.

5   **CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is a continuation-in-part under 37 CFR 1.53(b) to Application 10/663,955, "Direct Vial Surface Sorbent Micro Extraction Device and Method," filed on September 16, 2003 by Robert Wohleb.

STATEMENT REGARDING FEDERALLY SPONSORED
10   **RESEARCH OR DEVELOPMENT**

Not Applicable.

BACKGROUND OF THE INVENTION

Field of the Invention. This invention relates to the extraction of one or more analytes by a sorption process. Specifically, this invention relates to a device and method for
15   performing direct vial extraction and desorption. Additionally, this invention relates to a device and method for direct vial purification.

Description of the Related Art. To prepare samples for chemical analysis, often analytes, or the compound of interest, must be separated from a sample matrix, such as water, soil or animal tissue, and presented in a form suitable for a particular piece of analytical
20   equipment, such as a gas or liquid chromatograph. There are various extraction methods known and used to collect and prepare samples for such chemical analysis. These methods include liquid/liquid extraction, solid phase extraction, solid phase microextraction and stir-bar sorptive extraction. The new trend in the industry is toward simplified sample preparation that results in reduced waste and pollutants.

25   Liquid/liquid extraction partitions an analyte between two immiscible phases, such as an organic solvent and an aqueous phase. When an aqueous phase contains the analyte it is extracted into the immiscible organic solvent by placing the two phases into contact. Extraction is enhanced by mixing. A relatively large volume of solvent (typically greater than 100 mL) is necessary to carry out the extraction. Partitioning of a compound between the
30   solution solvent and extractant solvent is governed by the distribution constant, K, and the phase ratio, r. An example of such an extraction would be EPA test method SW846 3510 which specifies that one liter of aqueous sample should be serially extracted with 350 mL of methylene chloride. When the entire procedure is considered, a total of 500 mL of solvent is used for each sample. The solvent extract must be evaporated to reduce its volume to between

1 and 2 mL for placement into an autosampler vial prior to analysis.

Solid phase extraction (SPE) is often used to extract a sample prior to analysis by chromatography. SPE uses silica particles with an organic layer covalently attached to the surface of the particles. The silica particles are packed into a tube or disc, such as a polyethylene syringe barrel. The sample is then prepared and an analyte extracted by passing the sample through the solid sorbent. The analyte is then desorbed from the SPE media by solvent extraction. An example of such an extraction is EPA test method SW846 3535 which utilizes one liter of sample but requires approximately 50 mL of solvents. The solvent extract must be evaporated to reduce its volume to between 1 and 2 mL for placement into an autosampler vial prior to analysis.

It is known in the art to use a sorbent to extract an analyte from a solution. The analyte is later extracted from the sorbent by thermal desorption or by back extracting with a small amount of organic solvent. Sorption materials are usually homogenous, non-porous materials that are above their glass transition point (T_g) and in which the analyte can dissolve. The sample may be removed for analysis by thermal desorption or solvent extraction.

Solid phase microextraction (SPME) is an extraction technique wherein a fiber is coated with a sorbent layer. The coating may be a polysiloxane or other immobilized sorbent. The fiber is immersed in a liquid or exposed to its headspace during which time the analyte is retained. The fiber may then be inserted into a gas chromatograph injection port for analysis where it is thermally desorbed or may be back extracted with a suitable solvent. SPME is not accepted for EPA test methods.

Stir-bar sorptive extraction (SBSE) is used primarily for direct mode sampling. SBSE utilizes a thick sorbent coating on a magnetic bar stirrer that stirs the sample for a predetermined amount of time during which time the analyte partitions between the stir-bar sorbent and the sample. After extraction, the stir-bar is removed and the analyte is thermally desorbed to the injection port of a gas chromatograph.

Additionally, a sample may contain contaminants that interfere with analysis of the sample. Thus, it may be desirable to purify the sample by removing the contaminants before attempting to extract the analyte. SPE is commonly used to remove contaminants, with a particulate material, such as silica, packed in the barrel. As previously discussed, SPE requires large amounts of solvent and particulate material.

Examples of the prior art follow:

U.S. Pat. No. 5,691,206, issued to Pawliszyn on November 25, 1997 discloses a device for carrying out solid phase microextraction. The device is a fiber, solid or hollow,

contained in a syringe. The syringe has a barrel, a plunger slidable within the barrel and a hollow needle extending from the end of the barrel opposite the plunger. The needle contains the fiber. When the plunger is depressed, the fiber extends beyond a free end of the needle and when the plunger is in a withdrawn position the fiber is located within the needle. To
5   collect a sample, the needle is inserted through a septum in a bottle containing the sample and the fiber is extended into the sample. After a predetermined amount of time, the fiber is returned to the needle and the syringe is withdrawn from the bottle. The sample is analyzed by inserting the needle through a septum in a gas injection port of a gas chromatograph and extending the fiber.

10   U.S. Pat. No. 5,565,622, issued to Murphy on October 15, 1996 discloses a simplified method for solid phase extraction of components of interest from a sample. A syringe is used in which the inner surface of the cannula or needle is at least partially coated with a stationary phase such that aspirating the sample into the needle results in adsorption of the components of interest into the stationary phase. Aspiration of a solvent may be employed for removing
15   the components of interest from the stationary phase for direct injection into a chromatographic instrument, or the components of interest may be removed by thermal desorption, wherein the needle is placed in the injection port of the chromatographic instrument and heated. Because adsorption occurs on the inner surface of the needle, the components of interest are not readily storable.

20   U.S. Pat. Application Pub. No. US 2002/0105923, applied for by Malik, published on October 17, 2002 discloses a method of preconcentrating trace analytes by extracting polar and non-polar analytes through a sol-gel coating. The sol-gel coating is either disposed on the inner surface of the capillary tube or disposed within the tube as a monolithic bed.

Canadian Pat. No. 2,280,418, issued to Forsyth on February 12, 2001, discloses a
25   technique for carrying out solid phase microextraction of analytes contained within a liquid, solid or other material. A fiber assembly is mounted in the headspace of a gas-tight container. A coating is applied to the fiber assembly based on selectivity of the coating towards at least one analyte present in the sample. The fiber assembly is exposed either in direct contact with the sample, or indirectly through contact with the gas present in the headspace of the
30   container. After exposure, the analyte-containing fiber is then desorbed so the desired analyte can be analyzed. There are two alternatives for desorption under Forsyth. The coating must be removed from the fiber through solvent swell. Once the coating has been removed, the coating is placed in an autosampler vial containing a portion of solvent. The coating is suspended in the solvent, which can result in contamination and interference with the

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autosampler. Additionally, while this method reduces the amount of solvent necessary in the prior art, this method still requires a greater amount of solvent than the present invention. Alternatively, the coating can be left on the fiber and the fiber can be placed in the autosampler vial with a portion of solvent. However, this method still presents problems with autosampler contamination and operation.

An article entitled, "Headspace Sorptive Extraction (HSSE)" was published on an unspecified date by Tienpont, B. et al. at http://www.richrom.com/assets/CD23PDF/d43.pdf. The article discloses a glass rod support coated with a sorptive coating and suspended in the headspace of a closed container, which contains the analyte-bearing sample. The glass rod remains suspended above the analyte-bearing sample until equilibrium is reached. The glass rod is then removed from the closed container and undergoes thermal desorption.

Therefore, it would be an improvement in the art to have a device in which the extraction may be performed and the analyte conveniently and transportably stored for later analysis. It would also be an improvement in the art to have a device that minimizes labor and equipment necessary for extraction and desorption. It would also be an improvement in the art to have a device in which desorption may be performed easily, in which the amount of solvent waste is reduced, and that minimizes interference with the autosampler. Additionally, it would be an improvement in the art to have a device that removes contaminants in a sample and reduces waste and equipment. It would also be an improvement in the art to have a device that performs both extraction and purification, thereby further reducing waste and equipment.

BRIEF SUMMARY OF THE INVENTION

The present invention comprises a device and method for extracting analytes and/or removing contaminants from a sample.

Accordingly, the objects of my invention are to provide, inter alia, a solid phase extraction system that:

- minimizes the amount of solvent used;
- minimizes the amount of labor required;
- minimizes glassware;
- allows samples to be archived;
- allows extraction or purification to be performed at the sampling site rather than the laboratory;
- allows the extract to be subjected to replicate analysis;

- allows the use of gas or liquid chromatography autosamplers;
- allows the use of disposable sample vials;
- has greater reproducibility than solid phase micro extraction;
- eliminates interference with gas or liquid chromatography autosamplers;
- reduces or eliminates sample cross contamination;
- allows desorption of the analyte; and
- does not require expensive thermal desorption equipment.

This invention is a cap coated with either a sorptive coating or a particulate coating, wherein the coated cap is placed over an opening to a vessel containing a sample fluid. Upon exposure to the sorptive coating, the desired analytes are extracted from the sample. Similarly, upon exposure to the particulate coating, the contaminants are removed from the sample. The coated cap may be removed and replaced by an uncoated cap for transportation or storage of the sample. The analyte is then desorbed by attaching the sorptive-coated cap onto a vessel containing a portion of solvent and agitating the vessel.

Additionally, the particulate-coated cap may be used in conjunction with a sorption vial including a sorptive coating. Alternatively, a sorptive-coated cap may be used in conjunction with a particulate coated vial. When the sample comes in contact with the sorptive and particulate coatings, the particulate coating removes contaminants in the sample while the sorptive coating extracts the desired analytes.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-sectional view of the inventive cap.

Figure 2 is a cross-sectional view of a sample vessel.

Figure 3 is a cross sectional view of the inventive cap with a syringe-permeable membrane.

Figure 4A is a cross-sectional view of a screw cap.

Figure 4B is a cross-sectional view of a plug cap and sorption vial.

Figure 4C is a cross-sectional view of a snap cap and sorption vial.

Figure 4D is a cross sectional view of a crimp cap and sorption vial.

Figure 5 is a cross sectional view of a coated sorption vial.

DESCRIPTION OF THE INVENTION

Referring to Figures 1-2, an embodiment of the inventive cap is depicted as 300. Sidewall 301 and top cover 310 are integrally formed and define the boundaries of cap 300.

Sidewall 301 has sidewall exterior surface 302 and sidewall interior surface 324. Top cover 310 includes top cover exterior surface 312 and top cover interior surface 313. Top cover 310 has a cover periphery 316, which defines the boundary of top cover 310. Sidewall interior surface 324 and top cover interior surface 313 define cavity 330. Top interior surface 313 is

5   coated with either a sorptive coating or a particulate coating to create coated surface 322. Coated surface 322 extends into cavity 330. Top cover 310 may be solid, or may have a syringe-permeable orifice 319, as seen in Figure 3.

Referring to Figure 2, cap 300 is used to close vessel 100 at neck 140. Vessel 100 is used to provide an analyte-bearing sample 105 from which the analytes are to be extracted.

10   Vessel 100 is made from a rigid, nonreactive material, such as silica glass. Vessel 100 may be of any type, including various forms of flasks and vials known in the art. Vessel 100 defines enclosed chamber 110 wherein sample 105 is held, neck 140, and at least one vessel opening 102 through which sample 105 enters vessel 100. Neck 140 defines passageway 122. Opening 102 provides fluid communication from a sample source (not shown), through

15   passageway 122, and into chamber 110.

Neck 140 is configured so that cap 300 may attach to it and prevent fluid escape from chamber 110. Cavity 330 receives neck 140, and sidewall 301 holds top cover 310 over vessel opening 102 in a position preventing fluid communication between passageway 122 and the area external vessel 100. When cap 300 is attached to vessel 100, coated surface 322

20   faces chamber 110 of vessel 100.

Referring to Figure 3, an alternative embodiment of cap 300 is depicted. Syringe-permeable member 319 permits a needle (not shown) to pass through top cover 310. Syringe permeable member 319 is contiguously formed with top cover 310. Syringe permeable member 319 is semi-permeable and prevents fluid from escaping cap 300. However, a sharp

25   object (not shown), such as a syringe needle, can pierce through syringe permeable member 319 and enter cavity 330.

Various means may be used for interface between cap 300 and vessel 200. Cap 300 can be a screw-on type cap, a crimp cap, a stopper that plugs into neck 260, or a snap-on cap.

Referring to Figures 4A and 5, sidewall 301 is attached around cover periphery 316.

30   In one embodiment, sidewall 301 extends from top cover exterior surface 312, past coated surface 322 and on to sidewall end 308 distal coated surface 322. At least one cap thread 306 is helically attached along the cap interior surface 320 of sidewall 301. In this embodiment, cap 300 attaches to vessel 200. Neck 260 has at least one neck thread 264 helically attached around neck exterior surface 268. Cap thread 306 and neck thread 264 permit cap 300 to be

rotationally connected to neck 260.

In another embodiment, as depicted in Fig. 4B, sidewall 301 extends from cover periphery 316 to lower periphery 328. Cover periphery diameter 318 is larger than lower periphery diameter 329. Thus, sidewall 301 tapers as sidewall 301 extends from cover

5   periphery 316, past coated surface 322, and on to lower periphery 328. Cover periphery diameter 318 is larger than neck interior diameter 267, and lower periphery diameter 329 is smaller than neck interior diameter 267. Therefore, lower periphery 328 inserts into passageway 266 and top cover 310 is depressed until neck interior surface 263 snugly retains sidewall 301 in an interference fit.

10   In yet another embodiment, as depicted in Fig. 4C, sidewall 301 extends from top surface 312, past coated surface 322 and on to sidewall end 308 distal coated surface 322. Proximate sidewall end 308, sidewall 301 forms lip 304, which inwardly protrudes from cap interior surface 320. In order for engagement between cap 300 and neck 260, neck 260 provides rim 264. Cap 300 attachedly seals onto vessel 200 when top surface 312 is

15   depressed and lip 304 snaps over rim 264.

In yet another embodiment, as depicted in Fig. 4D, side wall 301 extends from top surface 312, past coated surface 322 and on to sidewall end 308 distal coated surface 322. At least one cap thread 306 is attached along cap interior surface 320 of sidewall 302 such that cap thread 306 is ring-shaped and has a smaller thread diameter 307 than sidewall diameter

20   303. To accommodate this embodiment, vessel 200 may have neck thread 264 around neck 260 with a larger neck thread diameter 265 than neck exterior diameter 261.

Referring to Figure 5, vessel 200 is defined by vial exterior wall 215 and vial base 250. Vessel 200 has a cylindrically-shaped interior wall 210 with a conically-shaped bottom surface 220. Vessel 200 also has a vial neck 260 through which there is an opening 262 to

25   bottom surface 220. Bottom surface 220 is oriented such that the vertex 224 of the conical bottom surface 220 is proximate vial base 250 while the directrix 226 is contiguous with interior wall 210. Either a sorptive coating or a particulate coating is applied proximate the vertex 224 of interior wall 210. Alternatively, vessel 200 can have a cylindrical interior wall 210 without a conical bottom surface. When vessel 200 has a cylindrical interior wall 210, a

30   coating may be applied at any point on interior wall 210.

In one embodiment of the invention, a sorptive coating and particulate coating are used in conjunction to extract analytes and purify the sample, respectively. Referring to Fig. 5, coated surface 222 is a particulate coating and is applied to interior wall 210 of vessel 200. Referring to Fig. 1, coated surface 322 is a sorptive coating and is applied to cap interior

surface 320 of cap 300. Sample 105 is introduced to vessel 200 via vial opening 262. Cap 300 is then attachedly engaged with vessel 200 by one of the methods discussed above. Vessel 200 is agitated by a mechanical shaker (not shown) for a predetermined period of time, exposing analyte-bearing sample 105 to the particulate and sorptive coatings. Sorptive

5   coating 322 sorptively extracts at least one analyte present in analyte-bearing sample 105, and particulate coating 222 removes at least one contaminant present in analyte-bearing sample 105. Cap 300 is removed and the remaining analyte-bearing sample 105 in vessel 200 is either archived or disposed. Cap 300 is then attached to a vessel 200, which is filled with solvent. The second vessel 200 is agitated for a predetermined period of time, allowing

10   desorption to occur. After desorption, the analyte-bearing solvent is ready for analysis.

Alternatively, coated surface 222 and coated surface 322 may each contain a particulate coating or a sorptive coating, as determined for a specific test.

In the preferred embodiment, the sorptive coating is a hydrophobic coating, such as an immobilized polysiloxane, for example polydimethylsiloxane (PDMS), which contains only

15   methyl functional groups. The name "siloxane" is based on the Si - O - Si unit and has found acceptance in scientific nomenclature. Polysiloxanes are polymers with repeating siloxane units. Each repeating siloxane unit contains two functional groups attached (e.g. dimethyl) which may, or may not, be of the same type of functional group. A functional group is an atom or combination of atoms which gives a polymer its distinctive and characteristic

20   chemistry. A polysiloxane of 50 repeating units would therefore have 100 methyl groups, whereas a siloxane unit with two different types of groups such as phenymethyl would have 50 of each "type" in the polysiloxane.

It is known in the art that immobilized polysiloxanes that contain other types of functional groups, may be used as sorbents. These include immobilized polysiloxanes

25   containing phenyl or trifluoropropyl functional groups. Examples of these polysiloxanes include diphenylsiloxane-dimethylsiloxane copolymers and trifluoropropylmethylsiloxanes. For more selective sorption applications the immobilized polysiloxane may contain other types of functional groups including alkyl, alkenyl, alkynyl, aryl, alkylaryl, alkenylaryl, alkynylaryl, haloalkyl or haloaryl. A polysiloxane may contain said types of functional

30   groups in any combination. The selection of the type of functional groups permits the partitioning of a particular analyte or analyes from the sample The polysiloxane coating may be a polymer, a copolymer or a combination of polymers.

Alternatively, sorptive coating may be (1) a porous layer, such as a derivatized etched surface, (2) other immobilized polymers that are above their glass transition temperatures

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such as polybutadiene, (3) an immobilized porous polymer, such as divinylbenzene, ethyleneglycoldimethacrylate, and copolymers of divinylbenzene and ethyleneglycoldimethacrylate, polyethyleneimine, acrylonitrile, n-vinyl-2-pyrollidinone or 4-vinyl-pyridine, (4) a sol gel or (5) an immobilized adsorbent such as graphatized carbon

5   black. Sorptive coating may be any one of the coatings described or a combination of two or more of the alternative coatings. Additionally, sorptive coating may be derivatized silica beads. The silica beads are derivatized by octadecyl (C_{18}), octyl (C_8), butyl (C_4), sorbent quartenary amine (SAX), benzenesulfonic acid (SCX), aminopropyl, cyano, phenyl or carboxylic acid. The derivatized silica is immobilized by a fibrous mesh, or any other

10   mechanical means. The selection of the coating or coatings by one skilled in the art is dependent upon the analyte or analytes to be partitioned from sample.

       Acceptable particulate coatings for use in purifying a sample include molecular sieves, activated alumina, silica, silica gel, and ion exchange resins. The selection of particulate coating by one skilled in the art is dependent upon the contaminants targeted and the analytes

15   present in the sample.

       The foregoing disclosure and description of the invention is illustrative and explanatory thereof. Various changes in the details of the illustrated construction may be made within the scope of the appended claims without departing from the spirit of the invention. The present invention should only be limited by the following claims and their

20   legal equivalents.